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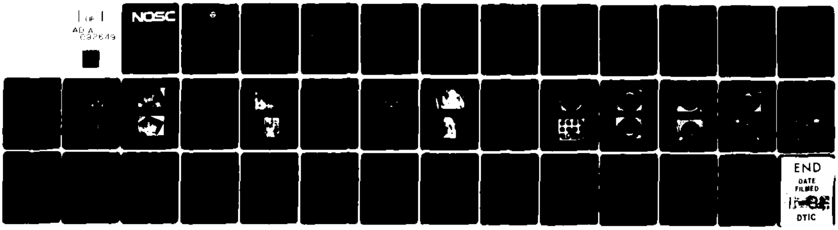

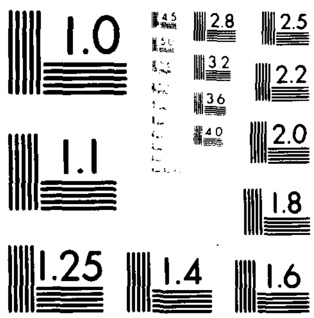

MICROCOPY RESOLUTION TEST CHART

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Technical Report 572

RESISTANCE OF COATED AND UNCOATED IR WINDOWS TO SEAWATER CORROSION, PHASE 2

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July 1980

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NAVAL OCEAN SYSTEMS CENTER
SAN DIEGO, CALIFORNIA 92152

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Germanium and chalcogenide glass specimens were submerged to a depth of 35 ft. in the San Diego Bay for 120 days and the deterioration of their surfaces noted. The germanium specimens were protected with single-layer and multilayer AR coatings, and the chalcogenide specimen was bare. To simulate a submarine operational scenario, the specimens were periodically brought above the water surface, dried off, and exposed to sunshine.

Germanium protected by single-layer AR coatings corroded as a result of pinholes in the single-layer coatings; however, the average transmittance of the better single-layer AR coatings tested decreased less than 5 percent

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20. ABSTRACT (Continued)

from pre-submersion values. Multilayer AR coatings on germanium proved better, exhibiting no pinholes and at worst only erosion of the topmost coating layers. The best of the multilayer coatings tested (Exotic Materials 40100) showed virtually no effects of corrosion and no substantial transmittance decrease in the 8- to 13-micron range. The Amorphous Materials, Inc. (AMTIR) chalcogenide glass also showed excellent results, exhibiting no significant corrosion or drop in transmittance.

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SUMMARY

PROBLEM

Germanium windows are to be used on submarine-mounted infrared imaging systems and thus will be immersed in seawater during most of their operational life. Since germanium corrodes in seawater, some method of protection is required. This protection must not, however, interfere with the function of the imaging systems. Rather, if feasible, it should assist in the performance of that function. Therefore, the protective coating on the external surface of the window must enhance, not impede, the transmission of electromagnetic radiation in the 7- to 13-micron spectral wavelength range. Also, it is desirable that the selected coating retard the biological fouling of the windows that otherwise would reduce transmittance.

APPROACH

An experimental approach to the problem was taken involving the testing, under conditions approximating those experienced in actual submarine missions, of various types of coatings on specimens fabricated from germanium and chalcogenide glass. This testing was an adjunct to previous similar coating evaluation studies (see Refs. 1 and 2).

The specimens tested were of six types: solid AMTIR* glass; germanium with single-layer antireflective (AR) coatings by Optic Electronic, Exotic Materials, and Optical Coating Laboratory, Inc. (OCLI); and germanium with multilayer AR coatings by Exotic Materials Co. and Optic Electronic.

The testing took place in San Diego Bay from 26 April to 20 August, 1979, off Berthing Pier 160, Naval Ocean Systems Center (NOSC), Bayside, at a depth of 35 ft.

RESULTS

The findings outlined below were made on the basis of data generated by test specimens wetted on a single face for 4 months by naturally circulating seawater at a depth of 35 ft. in San Diego Bay.

1. Germanium specimens coated with single-layer AR coatings corrode to varying degrees, depending upon the particular coating.

The specimens with the OCLI coating showed the greatest degree of pitting. However, the average transmittance loss in the 8- to 10-micron range was insignificant, only about 1 percent. At wavelengths in the 10- to 12-micron range the transmittance loss was slightly larger.

The Optic Electronic XF27 and the Exotic Materials 40104 AR coatings showed the best resistance to pitting, but of those two, only Exotic Materials 40104 showed insignificant loss in transmittance in the 8- to 12-micron range, while the Optic Electronic XF27 showed a 1- to 4-percent loss.

2. Germanium specimens coated with multilayer AR coatings did not exhibit pitting; however, some do deteriorate in varying degrees.

*Manufactured by Amorphous Materials, Inc.

The Optic Electronic XF127 and XF129 showed discoloration and deterioration of surface layers of the coatings, while the Exotic Materials 40100 showed no visible change. Also the post-submersion transmittance values for Optic Electronic XF127 and XF129 decreased significantly, while those of Exotic Materials 40100 showed no decrease from pre-submersion values in the 8- to 12-micron range.

3. Uncoated AMTIR chalcogenide glass did not corrode in seawater, and there was no measurable change in transmittance.

CONCLUSIONS

The specimens which showed the least surface deterioration and change in transmittance were: (1) germanium specimens coated with the multilayer Exotic Materials 40100 and (2) uncoated solid AMTIR chalcogenide glass specimens. The germanium specimens coated with single-layer AR coatings showed more deterioration and loss in transmittance, making them less suitable for underwater applications.

RECOMMENDATIONS

1. Germanium windows for marine service should be protected against corrosive action of seawater by multilayer AR coatings. Such coatings not only increase the transmittance of infrared signals over a wider range of wavelengths than do monolayer AR coatings, but also provide longer lasting protection to the surface of germanium than do monolayer AR coatings.

2. Hard coatings whose primary function is to protect germanium from seawater and only secondarily to reduce reflection of IR signals from the exterior surface of the window should be investigated. Prospective materials for such coatings are chalcogenide glass and carbon.

3. New military specification should be developed specifically for coatings that are transparent to IR signals and that will provide germanium optics with a minimum of 6 months' protection against corrosive action of seawater.

CONTENTS

INTRODUCTION

All infrared (IR) imaging systems operating in a marine environment require for their successful performance windows that, besides being transparent to IR radiation, are compatible with environmental parameters imposed by the marine environment. The environmental parameters inherent in submerged operations present a particularly difficult challenge to the designer of such a system as the window. For in addition to being transparent in the IR energy spectrum and resistant to saltwater corrosion, the system must also serve as a structural element of the pressure housing protecting the electro-optical imaging components from seawater intrusion. Because of the mismatch in coefficient of expansion, modulus of elasticity, and Poisson ratio, the mating of a pressure-resistant IR window to a metallic pressure housing requires a high degree of design sophistication derived from experience in this specialized area.

Even windows that successfully carry the structural loads imposed on them by hydrostatic loading must still endure the prolonged chemical attack of seawater on the highly polished surfaces exposed to the marine environment. Although germanium is not a very active chemical material, seawater reacts with it and forms soluble oxides and chlorides on its surface. For this reason, bare germanium windows cannot be used in marine service. The rough, corroded surface produced by seawater scatters and reflects incident thermal energy, significantly decreasing the magnitude of thermal signal strength transmitted through the window. The situation is not significantly different for most antireflective (AR) coatings* for germanium, or for protective overlays placed over the AR coatings. Thus, there are four options available to the designer:

1. Replace germanium with a more corrosion-resistant material transparent to infrared radiation.

2. Discover AR coatings with higher corrosion resistance.

3. Discover protective overlays transparent to IR energy that will protect the AR-coated windows for longer periods of submersion without decreasing overall transmittance.

4. Discover a coating that, although poor in AR qualities, possesses outstanding resistance to seawater corrosion.

All four options are promising approaches for prevention of corrosion on windows in IR imaging systems mounted on ships and submarines. If unlimited funding were available to the designer, all four approaches to corrosion prevention would be investigated, since it is not known where a technological breakthrough might occur. Because unlimited funding is generally not the case, the research effort has to be focused on only one, or at most two, approaches to the problem.

The two previous studies (Refs. 1 and 2) focused on the search for corrosion-resistant materials transparent to IR radiation and on protective plastic overlays for AR coated windows. The findings of these studies were: (1) protective plastic-film overlays do not provide long-lasting protection for germanium windows against seawater because of the film's inherent porosity and the occurrence of pinholes; (2) chalcogenide glasses provide outstanding resistance to seawater corrosion; (3) there is a large variation in the

*That is, coatings designed to minimize the inherent reflectivity of germanium.

longevity of the several AR coatings exposed to seawater; and (4) the best AR coating* among those tested will protect germanium windows for a minimum of 4 months.

As a result of these initial findings, it was decided to pursue further the approaches that appeared to be profitable and discontinue the one that showed few positive results. Thus the investigation into protective plastic overlays was terminated, the search for durable AR coatings expanded, and the evaluation of chalcogenide glass continued. It was hoped that by the end of this study phase a reliable estimate could be formulated on the maximum life expectancy of existing durable AR coatings on germanium windows and a confirmation could be obtained of the apparent immunity of chalcogenide glass to seawater corrosion.

STUDY PROCEDURE

OBJECTIVE

The objective of the study was to evaluate in the shortest possible time and with the smallest expenditure of funds the potential return on the two feasible approaches to extending the life of IR windows in marine service, i.e., by selection of more corrosion-resistant material or development of a more corrosion-resistant coating for germanium.

APPROACH

The approach to meeting the objective of the study was experimental. It allowed in the shortest possible time and with a minimum of expense the evaluation of the potential return on each of the two feasible technical approaches. It consisted of selecting representative samples from each group of candidate materials and submerging them in the ocean. At regular intervals, the specimens would be retrieved from the ocean and their condition noted.

SCOPE

The scope of the study was limited in number of test specimens, AR coatings, alternate materials, test conditions, and duration of submersion. As a result of these limitations, only the following potential approaches to increasing the life of IR windows in ocean environment were to be evaluated:

1. Alternate materials:
    a. Chalcogenide glass (AMTIR-1)
2. Competitive AR coatings for germanium:
    a. Single, durable AR coating applied to germanium by Exotic Materials, (Type 40104)
    b. Multilayer, durable AR coating applied to germanium by Exotic Materials, (Type 40100)
    c. Single-layer AR coating applied to germanium by Optic Electronic, (Type XF27)

*Monolayer AR coating (Exotic Materials Co. Composition #40104).

d. Multilayer AR coatings applied to germanium by Optic Electronic, (Type XF127 and Type XF129)

e. Single-layer AR coating applied to germanium by Optical Coating Laboratory Inc.

Corrosion resistance was evaluated on the basis of submersion for 4 months, the maximum duration of a projected submarine mission, while the ambient environment was limited to the condition of natural water circulation at a depth of 35 ft.

The selection of test specimens for this study was based primarily on the findings of an exploratory study conducted by the Naval Ocean Systems Center (NOSC) on a submerged platform off Berthing Pier 160, NOSC, Bayside, in the water of San Diego Bay (Ref. 1). The findings of this preliminary study showed that: (a) unprotected germanium surfaces corroded uniformly and the associated transmittance loss was close to 100 percent; (b) the Exotic Materials single-layer AR coating showed the best results, exhibiting the flattest transmittance curve over the desired spectral range prior to the testing and showing the smallest decrease in transmittance after exposure to seawater; (c) the plastic overlays tested degraded more rapidly than some of the bare AR coatings and had the additional shortcoming of reducing the initial transmittance of the specimens; (d) forced circulation decreased the amount of growth on the surface of the specimens, but led to a more rapid decay of some of the specimens' coatings (further testing and modification of this method of reducing marine growth must be conducted to make the method optimally effective); (e) the use of electric current to heat the windows and thereby discourage biofouling is not feasible without further testing and/or modification of the method of application of current; and (f) the unprotected chalcogenide glass (AMTIR-1) surfaces showed excellent resistance to seawater corrosion.

Thus, based on these findings, study was concentrated on improved single-layer and multilayer AR coatings as the approach offering the greatest potential return. Also, an AMTIR-1 specimen was again tested to see if the highly favorable results obtained previously could be repeated. The option of plastic overlays was set aside at this time because it had exhibited a low potential return. Further evaluation of methods of electrical-resistance heating and induced water circulation will take place prior to retesting.

TEST SPECIMENS

All specimens tested were 3-in.-diameter, ¼-in.-thick circular discs with polished faces (Fig. 1). There were 11 specimens of germanium with various coatings, and 1 specimen of AMTIR-1 glass. An inventory of specimens used is presented in Table 1.

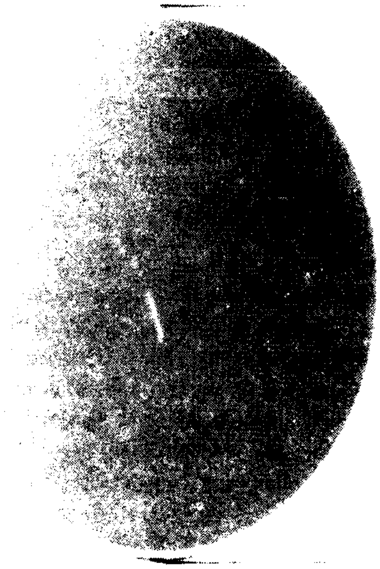


Figure 1. A typical test specimen.

Specimen Number	Manufacturer	Coating		Notes
		Sea Face	Dry Face	
58	AMTIR	No Coating	No Coating	Transmittance measured
39	Exotic Materials	AR, 40104	No Coating	Transmittance measured
63	Exotic Materials	AR, 40100	No Coating	
64	Exotic Materials	AR, 40100	No Coating	
71	OCLI	SLAR, P/N2	No Coating	Transmittance was measured for identical OCLI specimen, but not the one used in this test.
72	OCLI	SLAR, P/N4	No Coating	
73	OCLI	SLAR, P/N5	No Coating	
15	Optic Electronic	AR, XF 27	AR, XF 27	Transmittance measured
74	Optic Electronic	AR, XF 127	No Coating	Transmittance measured
75	Optic Electronic	AR, XF 127	No Coating	
77	Optic Electronic	AR, XF 129	No Coating	Transmittance measured
78	Optic Electronic	AR, XF 129	No Coating	

Table 1. Specimens tested in Fixture A: natural circulation.

TEST FIXTURE

The test fixture (labeled "A") held 12 specimens to be tested for fouling and corrosion by natural water circulation. The specimen holder for fixture A was a PVC sheet, 21.00 by 16.00 by 1.00 in. It had 12 evenly spaced recesses for specimens such that after mounting, the specimens would be flush with the surface of the PVC plate. Each recess had a ¼-in.-wide seat around its circumference, on which the specimen rested, and a shallow cavity below the specimen. The specimen holder had evenly spaced holes to accommodate the PVC studs used for fixture assembly.

Each specimen was placed in the fixture on a nylon-fiber-reinforced neoprene gasket that fit on the specimen seat. The specimen was then fastened watertight with an O-ring held down by a titanium ring clamp and fastened with nylon screws (Fig. 2).

PVC studs were placed through the specimen holder, and 3-in. tubular PVC spacers were placed over the studs.

Acrylic sheets, ½ in. thick, were placed on either side of the specimen holder as a protective cover for the specimens. These were drilled in the same manner as the specimen holder so that the studs would pass through them. The acrylic sheets were fastened in place with ½-in. PVC washers and hex nuts (Fig. 3).

The test fixture was fitted with aluminum angle stands by which the fixture could be attached to the testing platform with steel C-clamps. (Figs. 4 and 5).

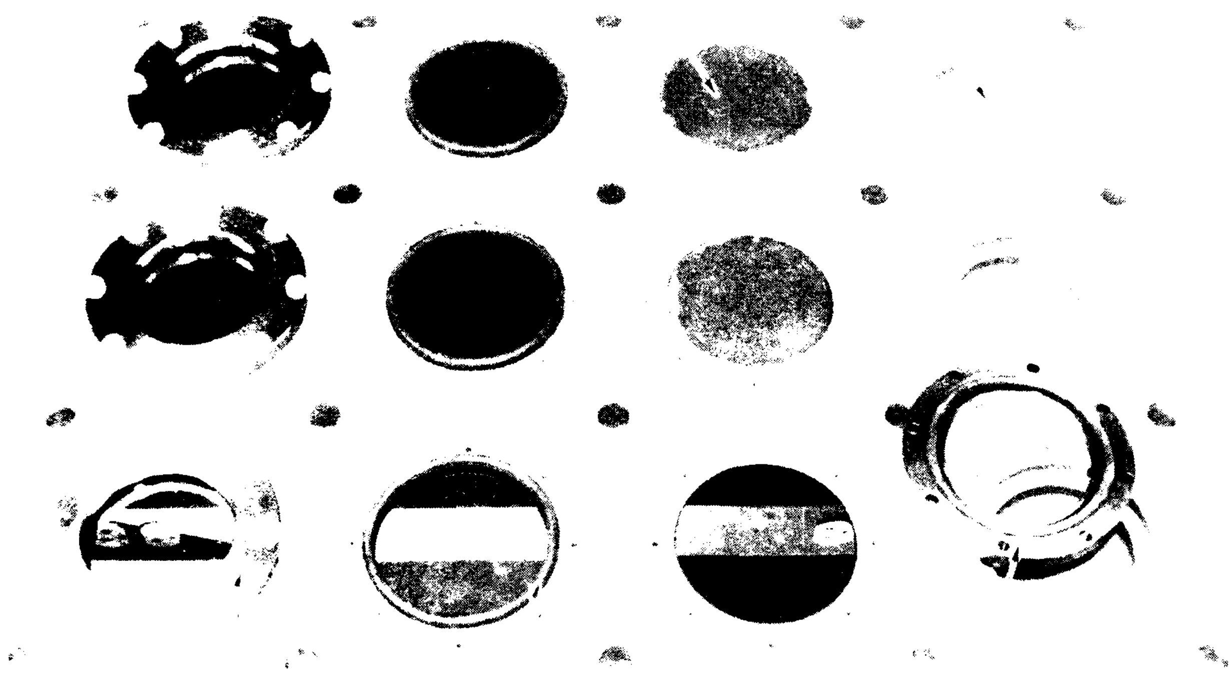
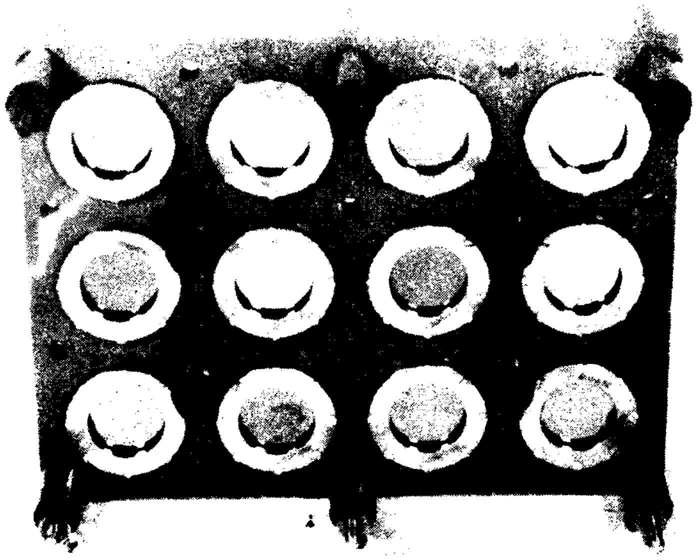


Figure 2. Test fixture A, partially assembled.



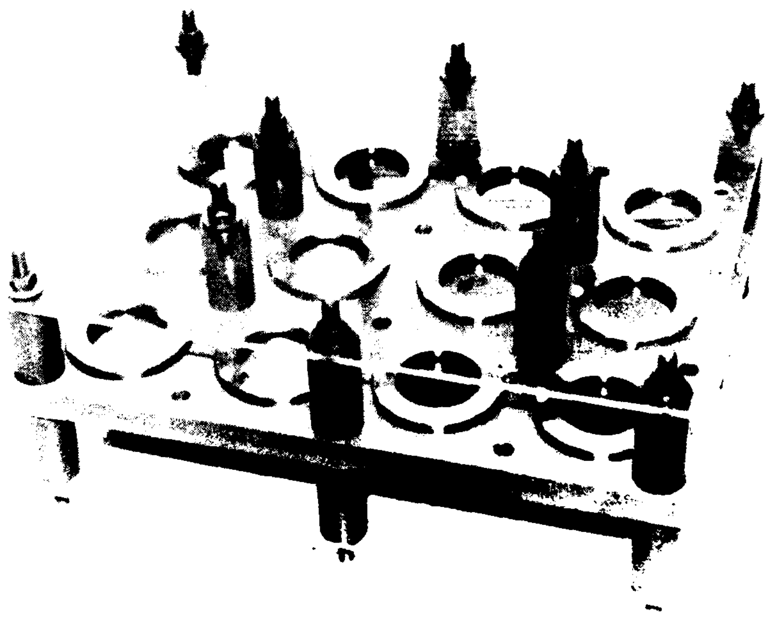


Figure 3. Fully assembled test fixture A (above), and the assembled test fixture with the front p[illegible]e removed, prior to immersion (below).

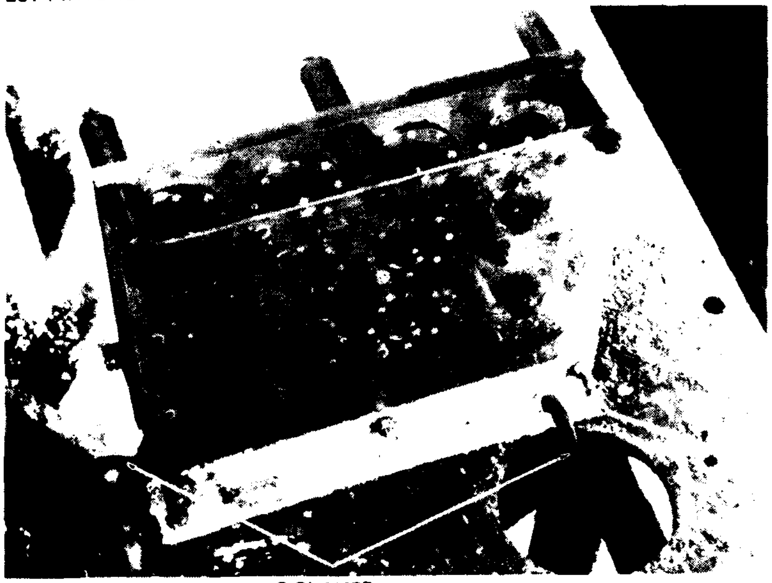


Figure 4. The assembled test fixture affixed to the testing platform, seen from Bldg 160, above the testing platform track which leads down to the water.

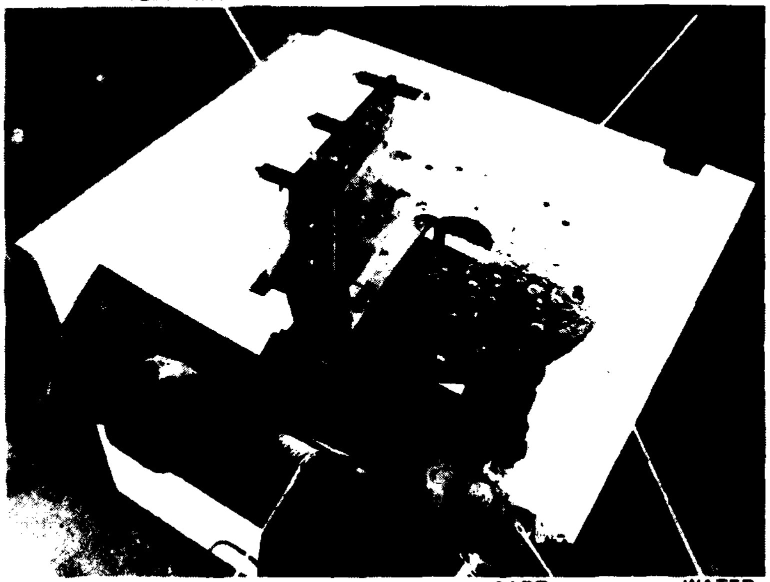


Figure 5. Test fixture A attached to the testing platform of the hydraulic hoist.

TEST ARRANGEMENT

The fouling test took place in the vicinity of Berthing Pier 160 and utilized the Sonar Facility, Building 160B, NOSC, Bayside. In this facility was housed a hydraulically operated hoist by which the specimens were lowered into San Diego Bay. The hoist had a flat platform to which the test fixture could be secured by the steel C-clamps. The platform was on a cart, which moved along tracks set at a 30-deg inclination to the water's surface (Figs. 6 and 7). The cart was raised or lowered by means of cables on a rotating drum driven by a hydraulic motor (Fig. 5).

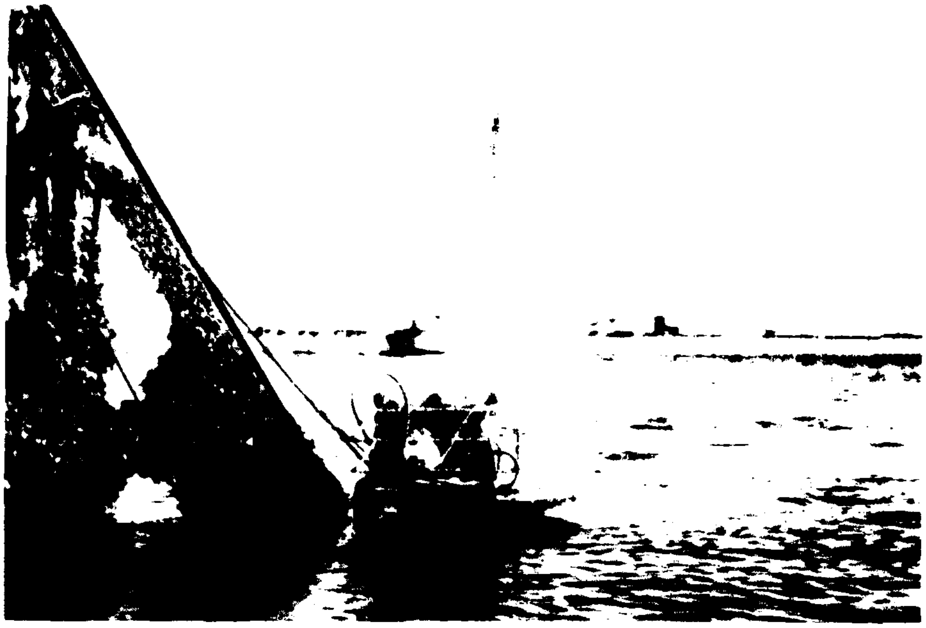


Figure 6. Testing platform and the tracks along which the platform is lowered into the water.

Figure 7. Closeup view of testing platform.

TEST PROCEDURES

The coated germanium specimens and the AMTIR-1 glass specimen were arranged in the fixture for data collection (Fig. 8), and the fixture was lowered into the bay. Testing commenced April 26, 1979. Data from each specimen were recorded, including the day of the test and qualitative observations regarding growth on and physical condition of the specimen. Further, the data included a description of ocean conditions, such as water temperature, tide-induced water circulation, water surface conditions, and sunlight conditions.

In the ensuing months of the test, the fixture was raised from the water two to three times a week and data of the type specified above recorded (Fig. 9). At approximately 1-month intervals, the test fixture was removed from the hoist and the protective acrylic front-plate removed from the fixture to facilitate photography. Each specimen was closely photographed to record its condition.

After the first month of testing, the specimens and fixture were hosed with tap water approximately once a week to remove the excess growth forms (Fig. 10). This was done to better simulate actual underwater conditions. In actual submarine conditions the specimens would not be in stagnant water, as they were in this test. In actual conditions the periodic extension of the sensor mast allows a flow of water past the window, which decreases the amount of growth on its surface. As a consequence there would not be the accumulation of growth that occurs in stagnant conditions. Therefore the specimens were hosed off to remove the growth and occasionally wiped with a soft cloth to remove stubborn growths.

After approximately 4 months, the testing was completed August 20, 1979. The specimens were thoroughly cleaned and inspected for damage, and representative samples were used for IR transmittance measurements.

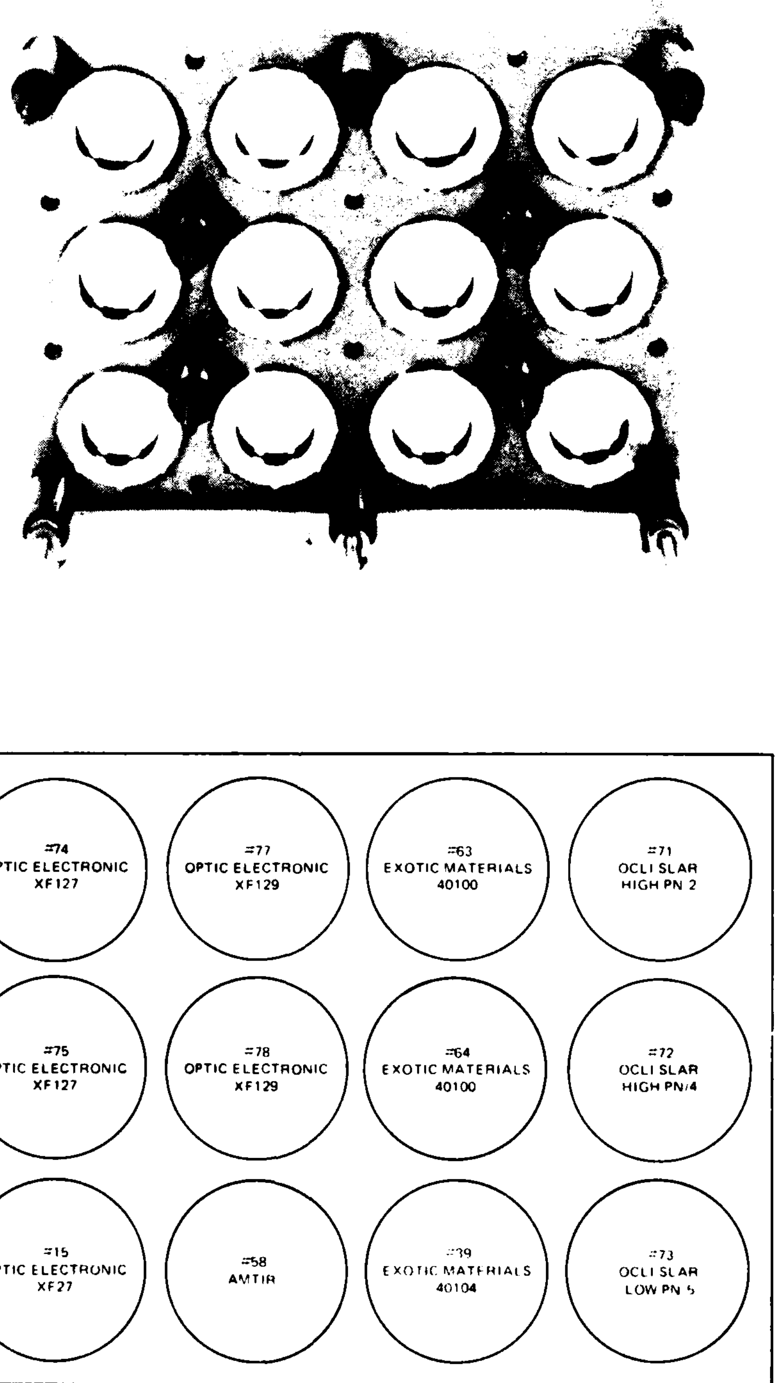


Figure 8. The test fixture (top) prior to immersion in San Diego Bay, and the placement of specimens (bottom).

Figure 9. Specimens are examined closely for the recording of data.

Figure 10. Specimen fixture and specimens are hosed with tap (fresh) water to remove excess growth

FINDINGS

GENERAL OBSERVATIONS:

During testing, the water temperature ranged from an average of 15.5°C in the first month to 20°C in the final month. It was not apparent that this temperature change or any daily temperature fluctuations within this range affected the results of the test.

Within the first month of testing, only the specimens with the Optic Electronic XF129 coating showed any sign of physical change (Fig. 11). Within 1 week of testing, these specimens developed a thin, greaselike film of a lighter hue than the specimens' coating. This film was removed by wiping with a soft cloth and did not recur. The specimens did, however, retain a slightly blotchy discoloration.

No other specimens showed any sign of corrosion or physical deterioration during the first month, although some growth had developed (Fig. 12). This growth was subsequently hosed off.

Throughout the following months the Optic Electronic XF129 showed increased discoloration. The appearance indicated that a darker upper layer of coating had worn off to reveal a lighter hued layer of coating underneath (Fig. 13). There was no visible pitting on the XF129 specimens at the conclusion of testing.

The Optic Electronic XF127 specimens also discolored in the ensuing months, showing a lighter hue under the darker surface. Both specimens were 75 to 85 percent discolored (Fig. 14) at the conclusion of testing.

The single-layer Optic Electronic XF27 did not have the discoloration problem of the multilayer Optic Electronic coatings. However, some spotting was noticed by the end of the second month (Fig. 15), and by the fourth month it was apparent that this spotting was the beginning of fine pinpoint pitting. At the end of the testing period, the XF27 specimen had some fine pinpoint pitting and several deeper scratches, perhaps caused by worm-like growths (Fig. 16).

The best results were obtained from the two specimens coated with Exotic Materials Multilayer Durable 40100 coating and the AMTIR specimen. None of these specimens showed any pitting, discoloration, or deterioration (Figs. 17 and 18).

The single-layer Exotic Materials 40104 coating, however, did not hold up as well as the multilayer 40100 coating. By the end of the second month (Fig. 19) some spotting became apparent, and by the completion of testing these spots were seen to be pinpoint pits (Fig. 20). These were evenly dispersed across the surface and very shallow. No discoloration of the specimen was apparent.

The deterioration of the OCLI single-layer AR coating was more severe than that of the Exotic Materials 40104 single-layer coating. The OCLI coatings showed discoloration by the end of the second month, and one specimen (no. 72) showed the first indications of pitting at this time (Fig. 21). All three OCLI specimens were pitted by the third month, and by the fourth month, the specimens' surfaces were 75 to 85 percent covered with pinpoint pitting. The pitting was concentrated at the center of each specimen (Fig. 22). None of the specimens had any visible discoloration at the termination of seawater exposure after 4 months.

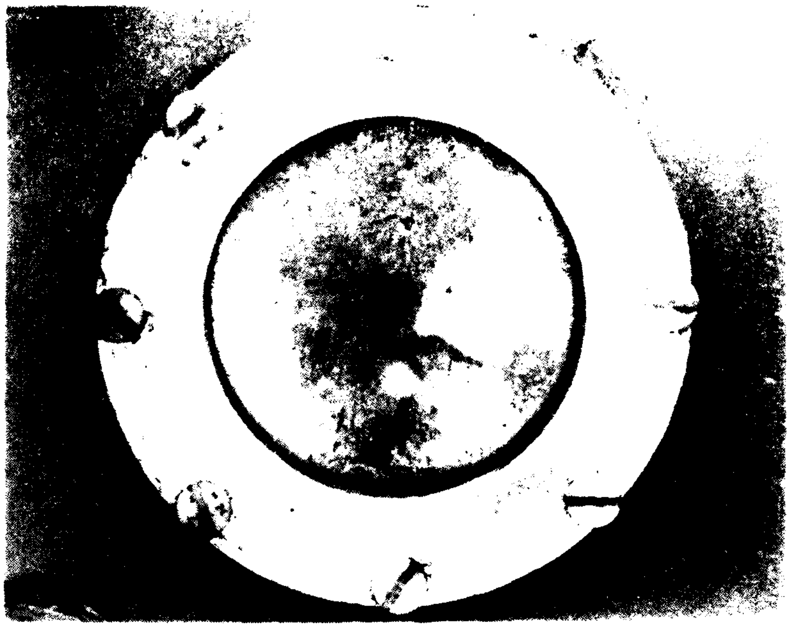


Figure 11. A germanium specimen with the Optic Electronic XF129 AR coating, after 1 month in San Diego Bay.

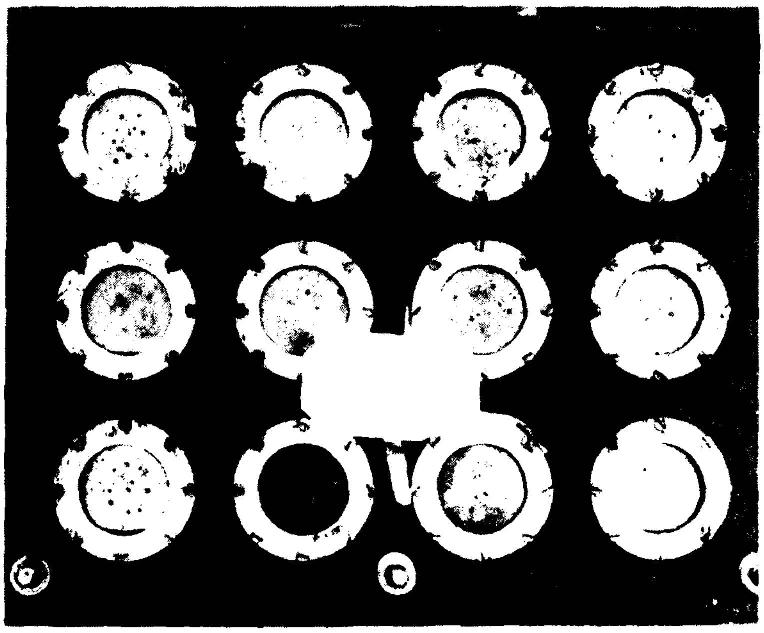


Figure 12. The test fixture after 1 month in the San Diego Bay.

Figure 13. A germanium specimen with the Optic Electronic XF129 AR coating, after 4 months in San Diego Bay.

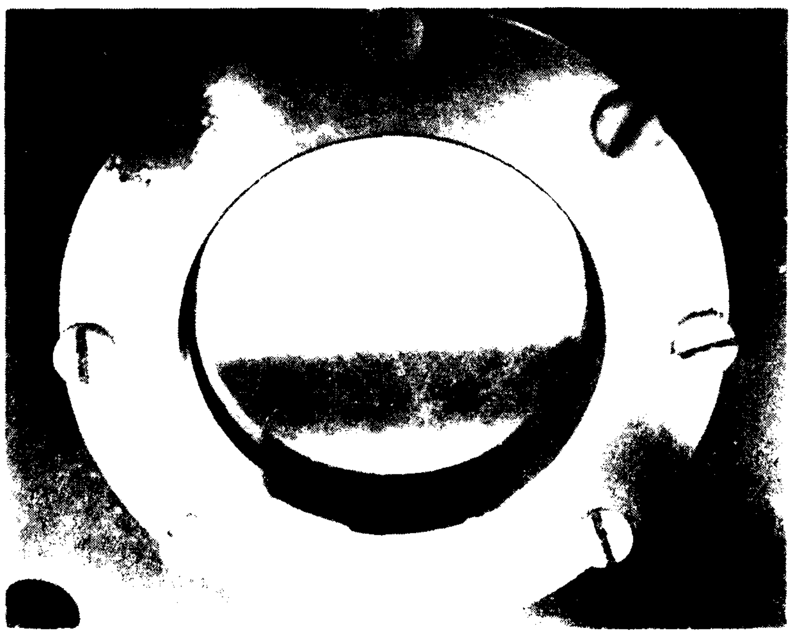


Figure 14. A germanium specimen with the Optic Electronic XF127 AR coating after 4 months in San Diego Bay.

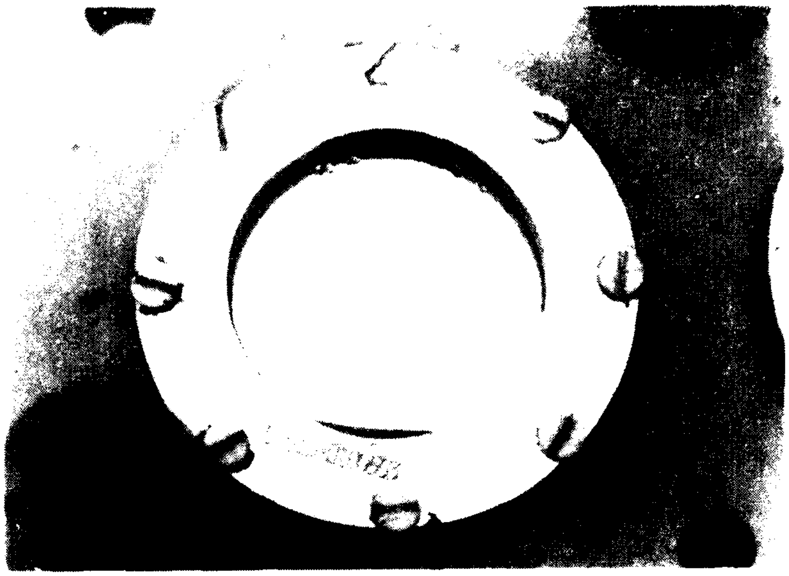


Figure 15. A germanium specimen with the Optic Electronic XF27 AR coating, after 2 months in San Diego Bay.

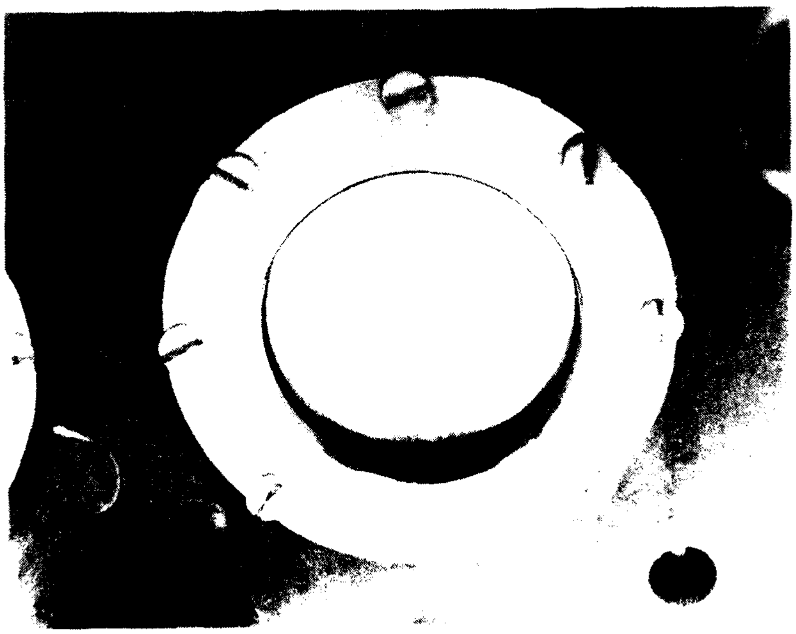


Figure 16. A germanium specimen with the Optic Electronic XF27 AR coating, after 4 months in San Diego Bay.

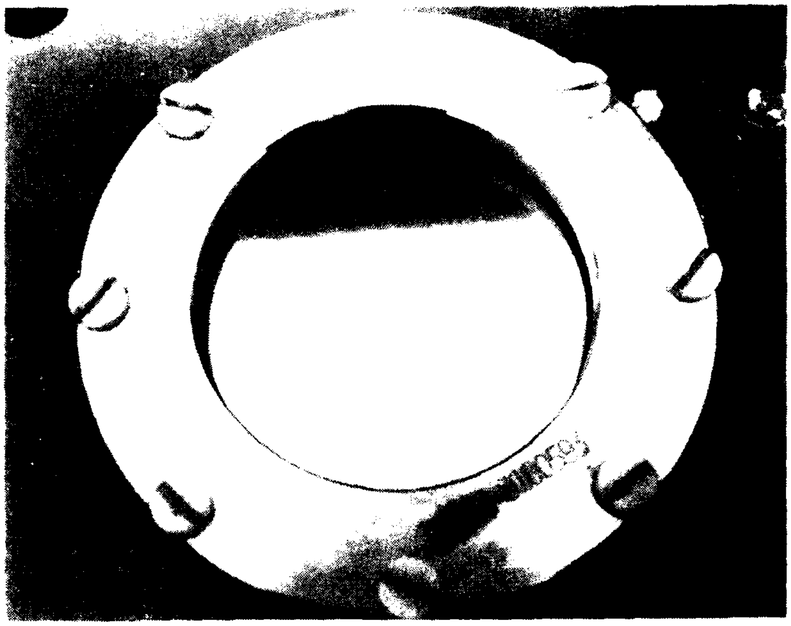


Figure 17. A germanium specimen with the Exotic Materials 40100 AR coating, after 4 months in San Diego Bay.

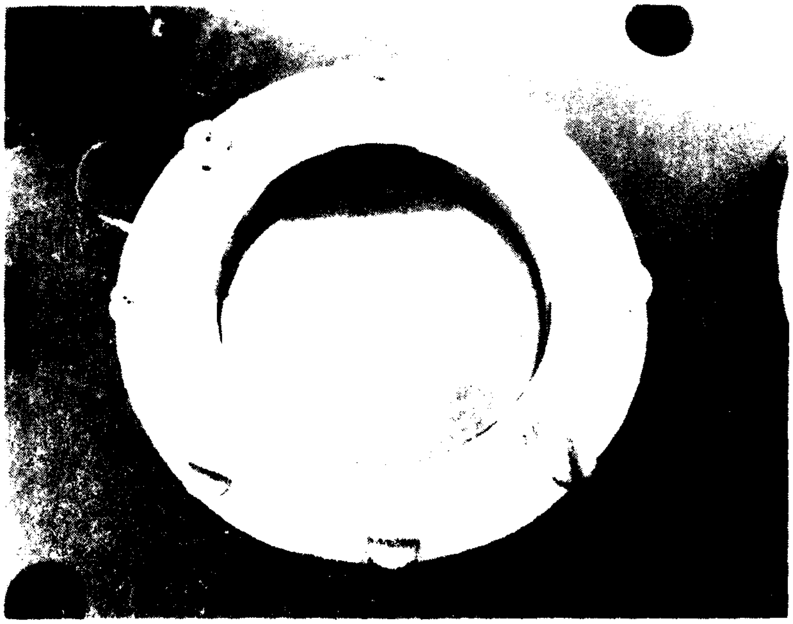


Figure 18. A specimen of AMTIR glass after 4 months in San Diego Bay.

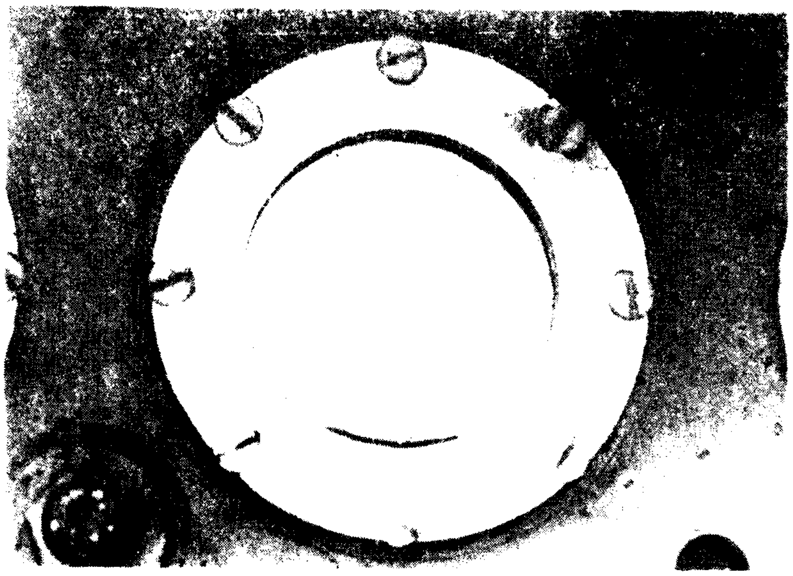


Figure 19. A germanium specimen with the Exotic Materials 40104 AR coating, after 2 months in San Diego Bay.

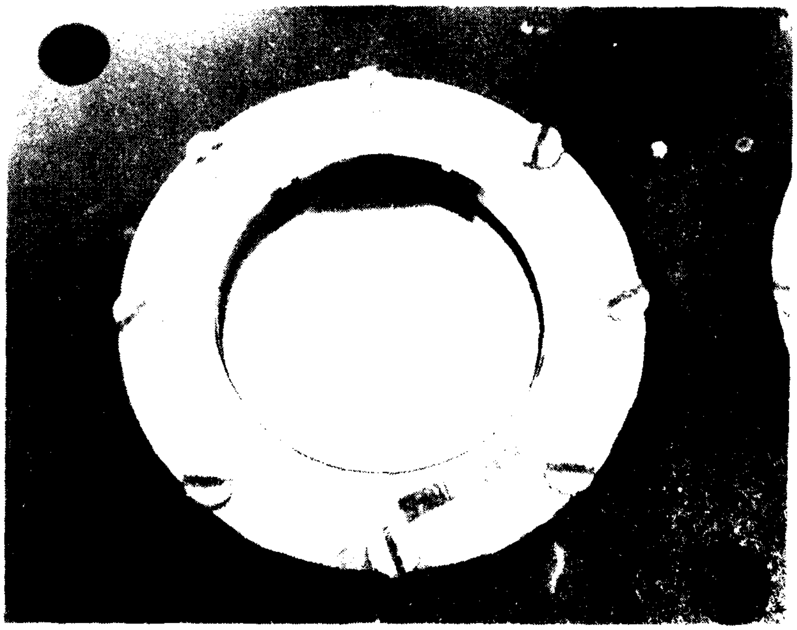


Figure 20. A germanium specimen with the Exotic Materials 40104 AR coating, after 4 months in San Diego Bay.

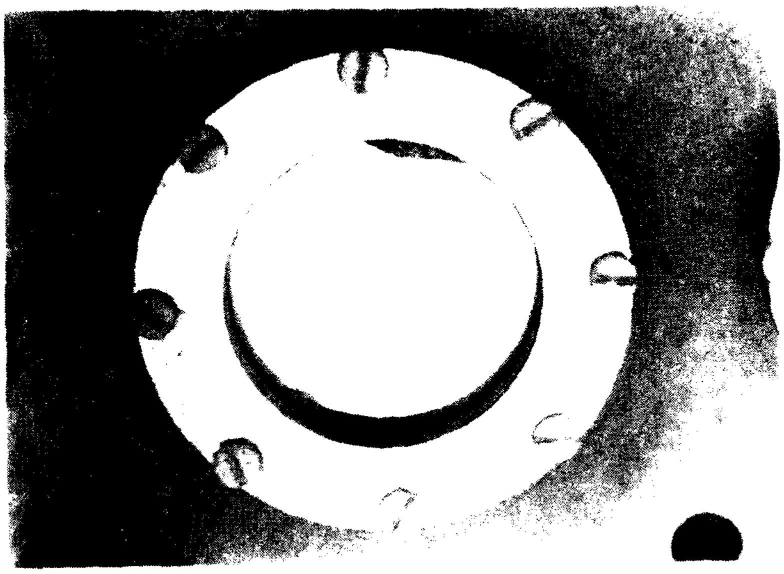


Figure 21. A germanium specimen with the OCLI single-layer AR coating, after 2 months in San Diego Bay.

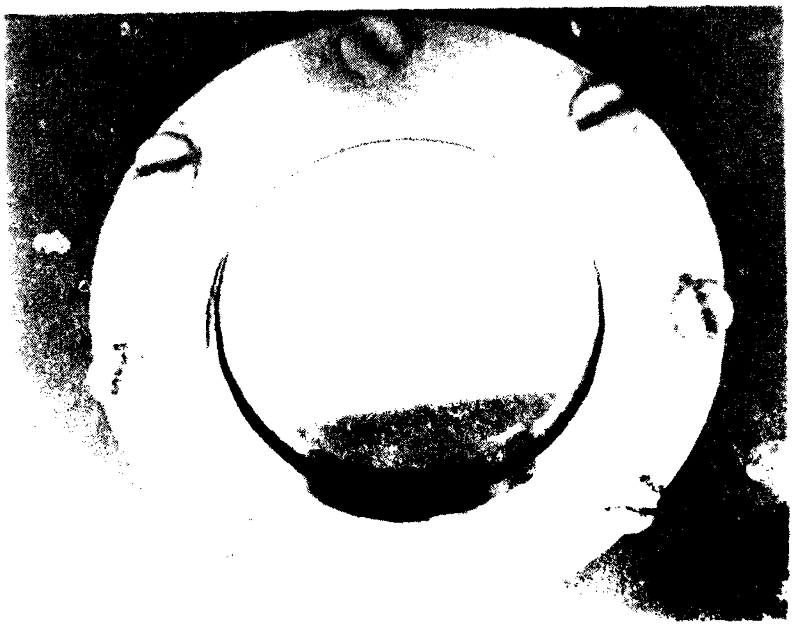


Figure 22. A germanium specimen with the OCLI single-layer AR coating, after 4 months in San Diego Bay.

TRANSMITTANCE MEASUREMENTS

Transmittance tests were performed on specimens of each coating type and on the AMTIR specimen to compare the effectiveness of the various surfaces prior to and after submersion in seawater. The specimens' surfaces were cleaned and dried prior to each measurement of transmittance. These measurements provide data only on the transmittance of electromagnetic radiation in the 8- to 14-micron wavelength range. The effect of surface deterioration on the MTF (mean transfer function) of the specimens was not measured. Thus the extent to which surface deterioration would be detrimental to the optical resolution of a thermal imaging system equipped with windows coated in the same manner as these test specimens is not known.

Generally speaking, measurements made before and after exposure to seawater showed no significant difference in specimen transmittance. The only major decrease in transmittance was in the lower wavelength range of the Optic Electronic XF127 coating.

SPECIFICS:

1. Uncoated Materials. There was no significant change in the transmittance of the AMTIR specimen after 4 months' submersion in seawater (Fig. 23). The transmittance averaged approximately 68% over the range 7 to 11 microns and gradually rolled off to approximately 55% at 14 microns. The small increase in transmittance measured on specimens after submersion is within precisional limits of the testing apparatus. Moreover, the small increase could also possibly be due to a small amount of oxidation on the weathered surface, which would act as an AR coating.

2. Single-Layer AR Coatings. Of the single-layer AR-coated specimens, the Exotic Materials 40104 showed the smallest change in transmittance after 4 months' exposure to seawater. The transmittance of specimens coated on one surface was about 60 to 65% in the 8- to 11.5-micron range and rolled off to approximately 45% at 14 microns (Fig. 24). The difference between the measurements made before and after submersion is small enough to be within the range of instrument error and therefore of no significance.

After submersion, the Optic Electronic XF27 transmittance curve dropped by approximately 5% in the 9- to 10-micron range and by approximately 4% in the 12- to 14-micron range (Fig. 25). This was a small drop, but slightly larger than can be accounted for by instrument error. The average transmittance of specimens coated on both surfaces was seen to peak at approximately 9.5 microns and then decrease with increasing wavelength. The range was approximately 90% transmittance at 8 microns and approximately 60% at 14 microns, with a peak of 93% at approximately 9.5 microns.

Similarly, the decrease in transmittance of the specimens coated with single-layer SLAR OCLI AR coating varied with wavelength of IR signal (Fig. 26). After 4 months, transmittance in the 8- to 12-micron range showed no difference (within instrumental precision) from the pre-submerged value but began to decrease with increasing wavelength. At a wavelength of 14 microns, the post-submersion transmittance was approximately 8% lower than the pre-submersion value of about 56%.

3. Multilayer AR Coatings. Of the three multilayer AR coatings, the Exotic Materials 40100 showed the best transmittance after 4 months' submersion. The transmittance after submersion was the same, within precision limits, as the pre-submersion transmittance (Fig. 27) in the 8- to 13-micron range. For specimens coated on one surface,

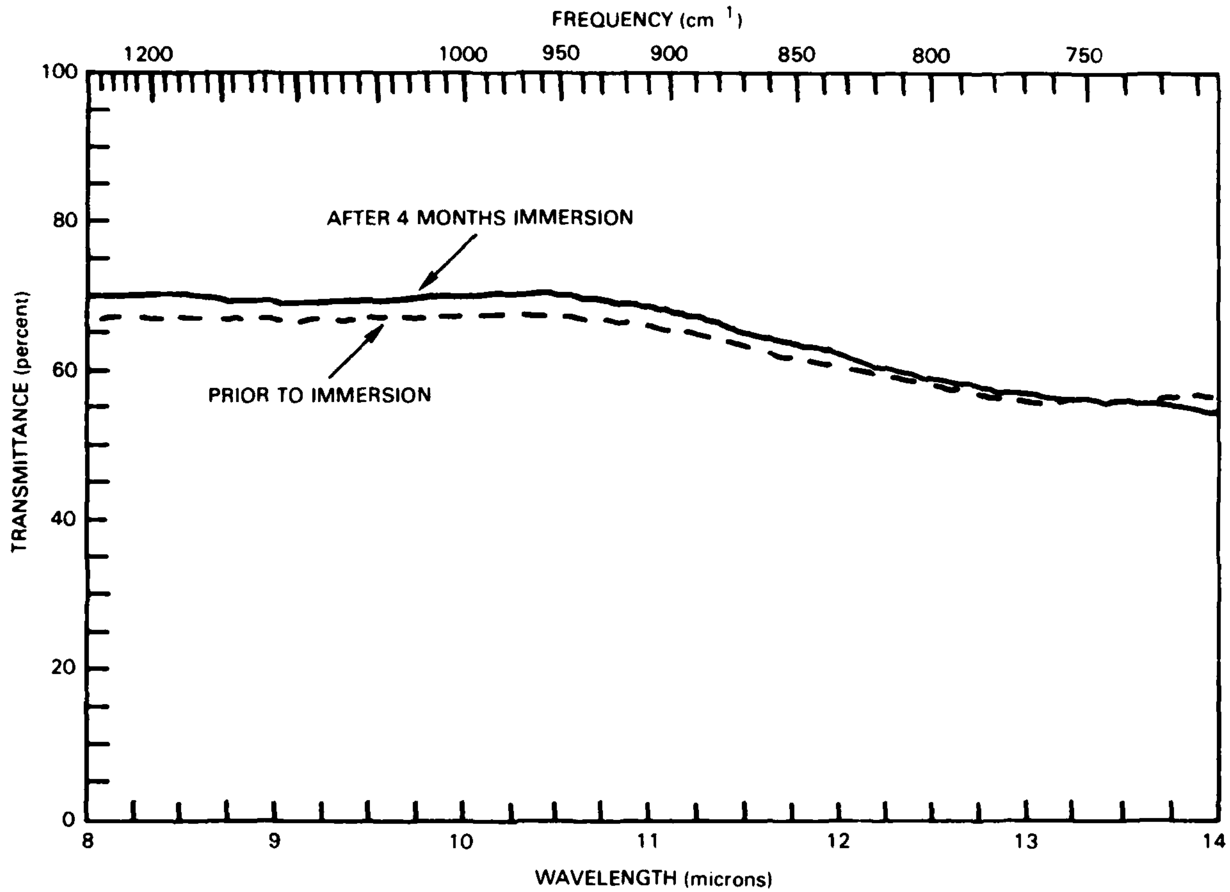


Figure 23. A plot of percent transmittance versus wavelength for the AMTIR glass specimens both prior to and after immersion in seawater 26 April 1979 to 20 August 1979.

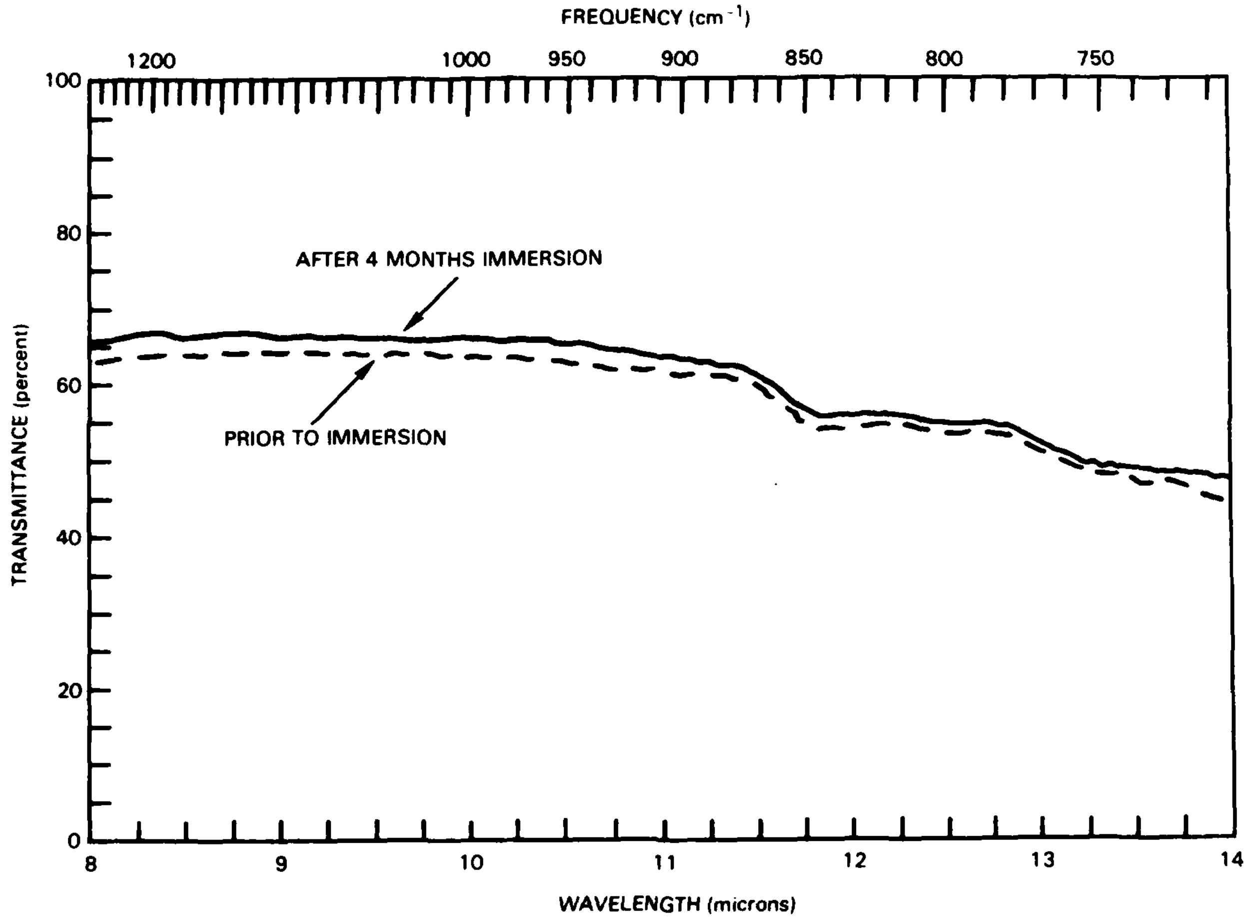


Figure 24. A plot of percent transmittance versus wavelength for a germanium specimen with the Exotic Materials 40104 single-layer AR coating, both prior to and after immersion in seawater from 26 April 1979 to 20 August 1979. Specimen coated on wetted surface only.

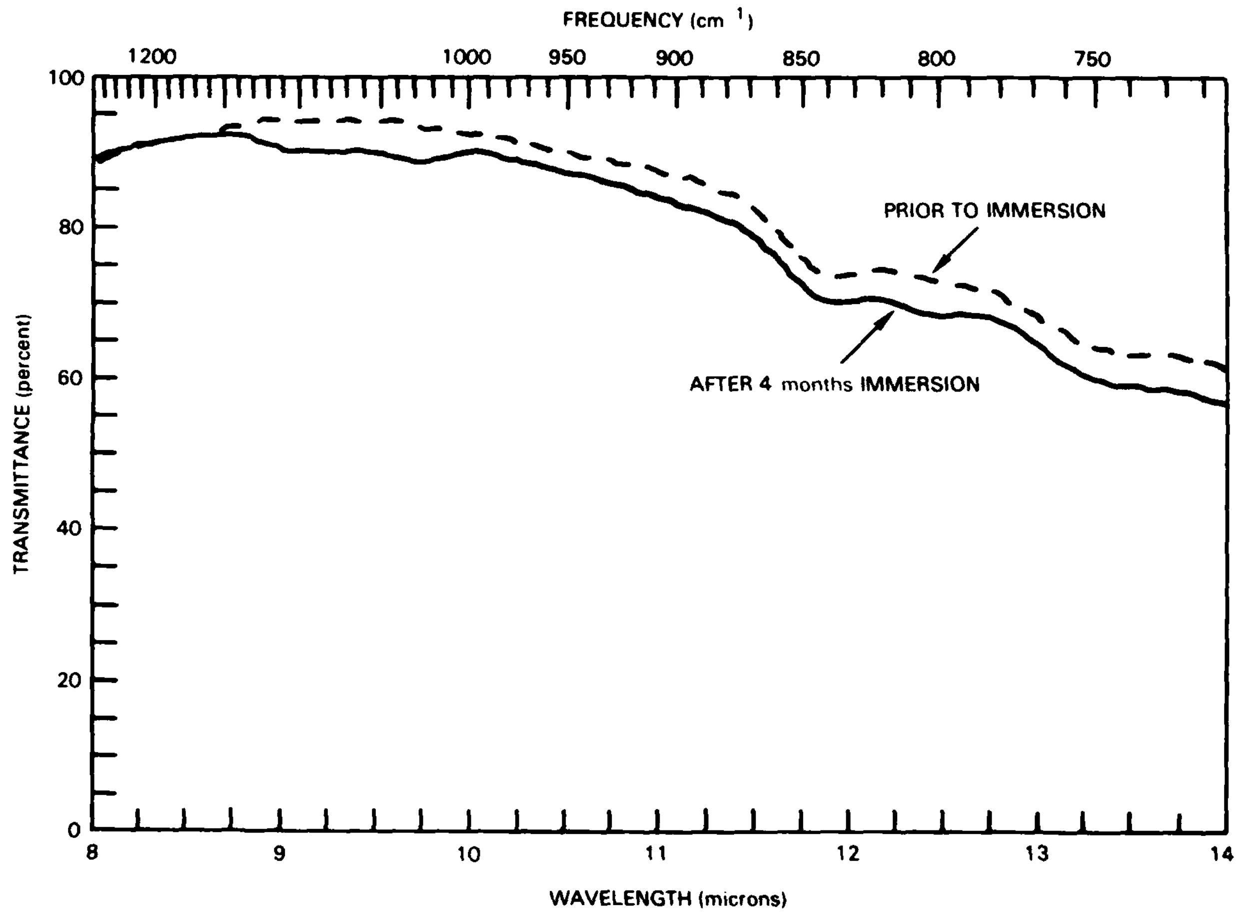


Figure 25. A plot of percent transmittance versus wavelength for a germanium specimen with the Optic Electronic XF27 single-layer AR coating, both prior to and after immersion in seawater from 26 April 1979 to 20 August 1979. Specimen coated on both surfaces.

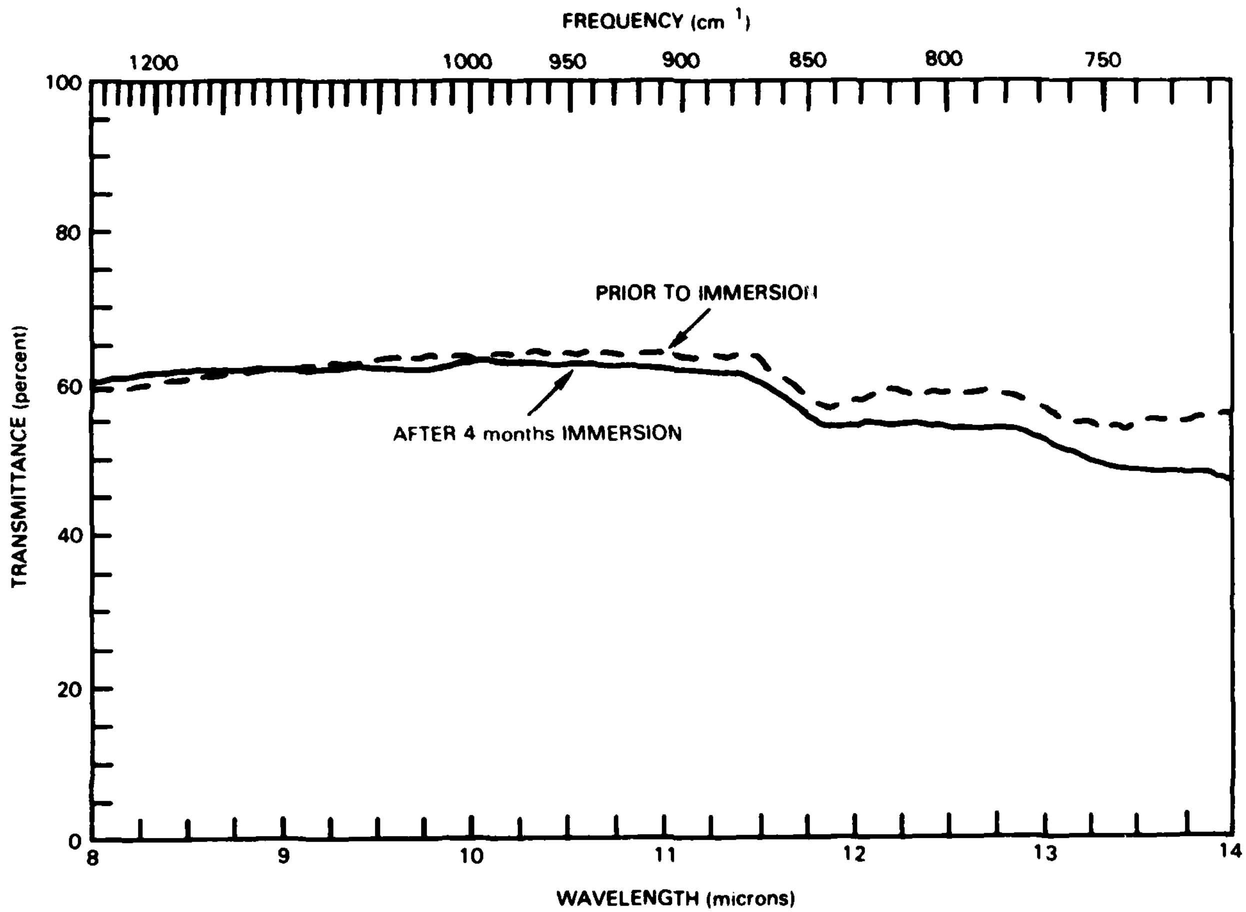


Figure 26. A plot of percent transmittance versus wavelength for a germanium specimen with the OCLI single-layer AR coating, both prior to and after immersion in seawater from 26 April 1979 to 20 August 1979. Specimen coated on wetted surface only.

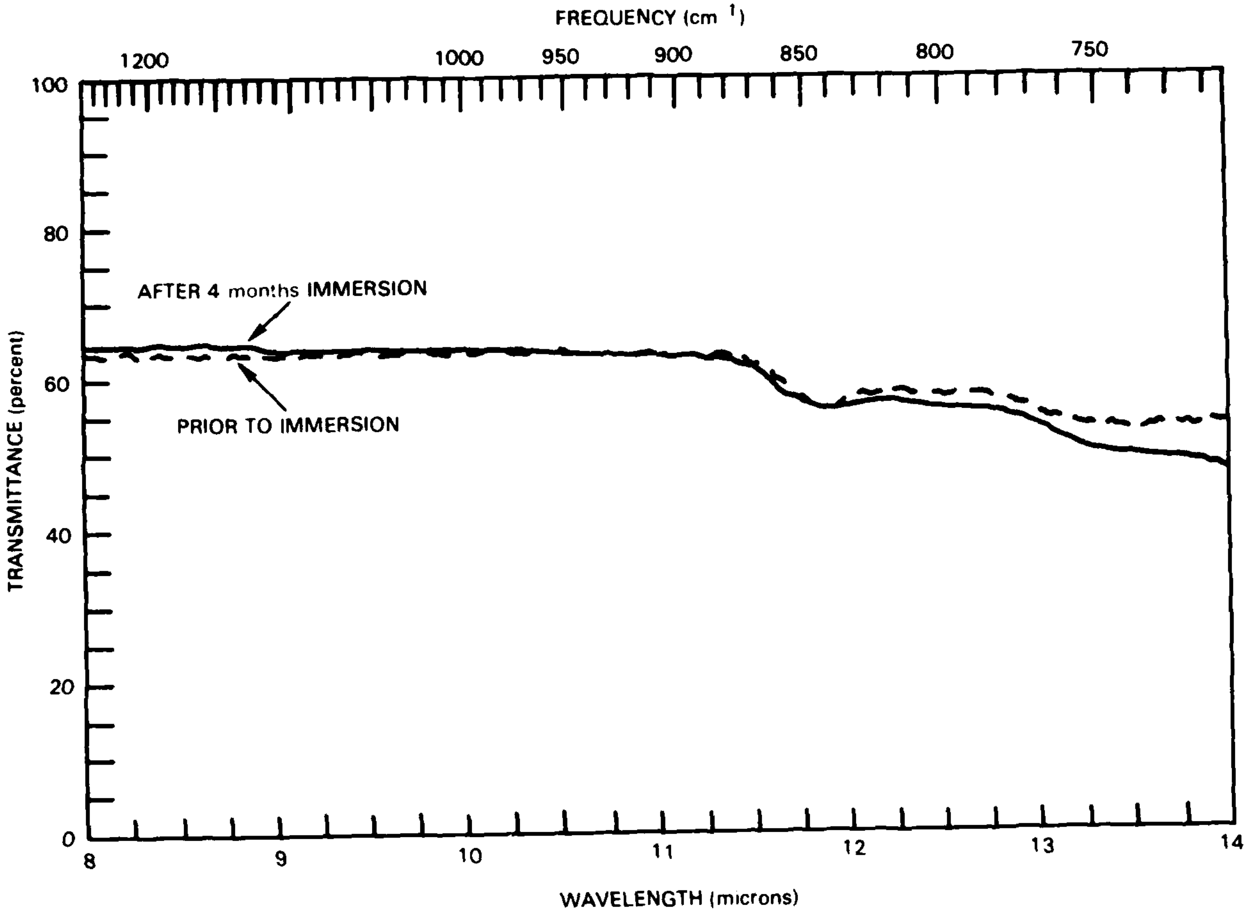


Figure 27. A plot of percent transmittance versus wavelength for a germanium specimen with the Exotic Materials 40100 multilayer AR coating, both prior to and after immersion in seawater from 26 April 1979 to 20 August 1979. **Specimen coated on wetted surface only.**

the transmittance was 60 to 65% in the 8- to 11.5-micron range, sloping off to about 50% at 14 microns.

The Optic Electronic XF129 transmittance dropped slightly after 4 months' submersion, with a maximum drop of approximately 4% around 9.5 microns (Fig. 28) from the pre-submersion level of approximately 50%. The transmittance of specimens coated on one surface varied from approximately 50% at 8 microns to 35% at 14 microns after submersion.

The Optic Electronic Multilayer coating, XF127, showed the greatest drop in transmittance of all the specimens tested (Fig. 29). At the end of testing, the transmittance of specimens coated on one surface had decreased 10% from their pre-submersion value of approximately 64% at the lower end of the range (8 microns). However, by 11.5 microns the value approached equivalence, within precision limits, with the pre-submersion values of 50 to 55% transmittance. The curves rolled off to approximately 42% transmittance at 14 microns.

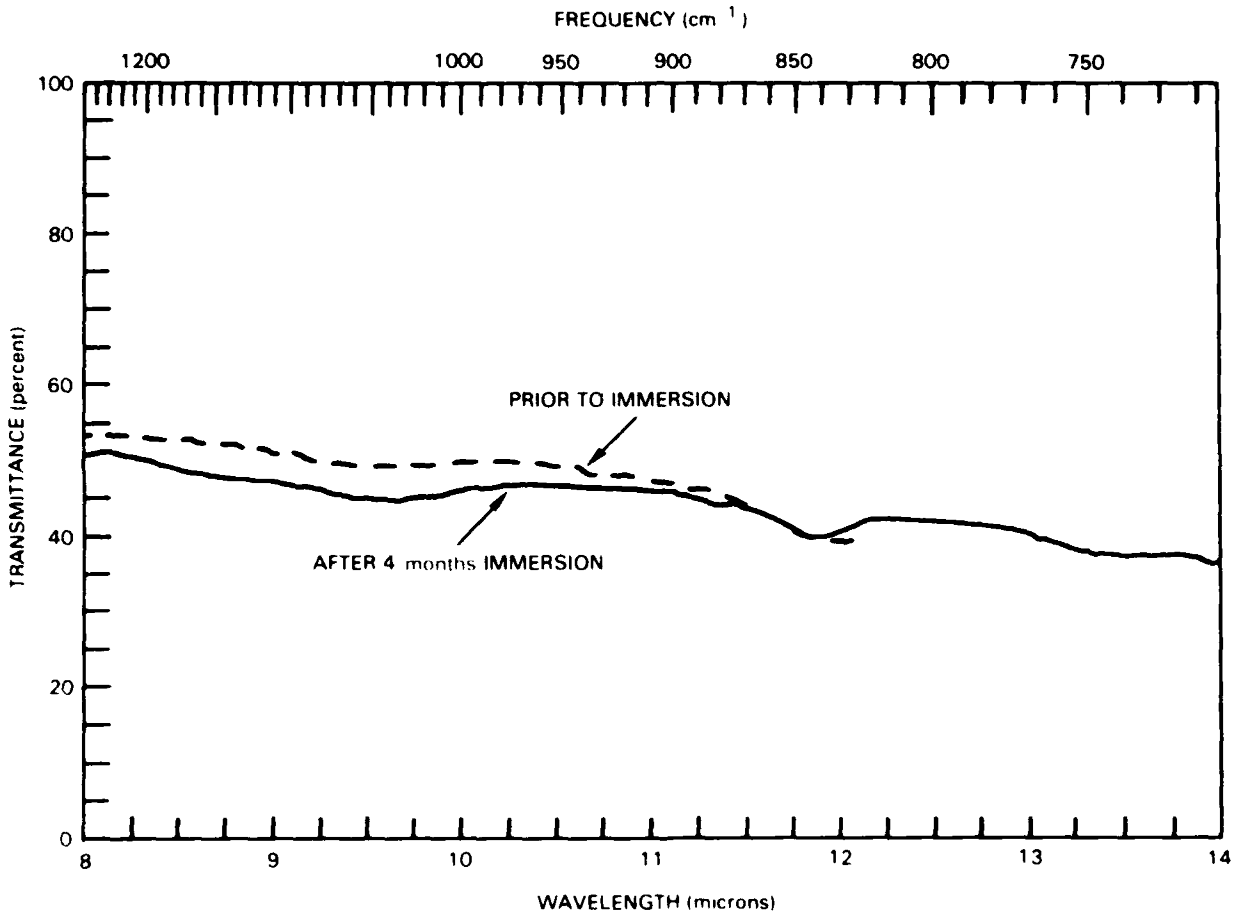


Figure 28. A plot of percent transmittance versus wavelength for a germanium specimen with the Optic Electronic XF129 multilayer AR coating, both prior to and after immersion in seawater from 26 April 1979 to 20 August 1979. **Specimen coated on wetted surface only.**

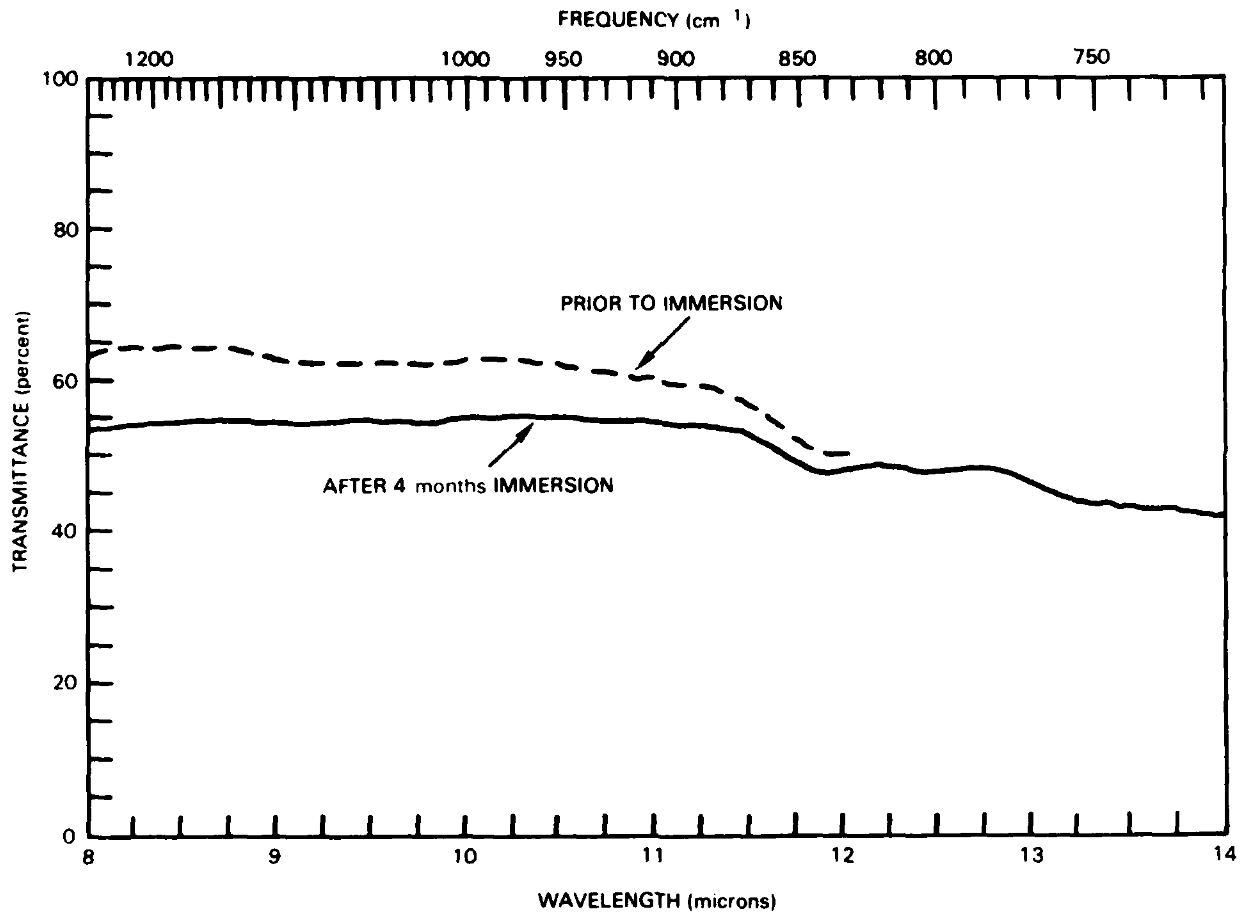


Figure 29. A plot of percent transmittance versus wavelength for a germanium specimen with the Optic Electronic XF127 multilayer AR coating, both prior to and after immersion in seawater from 26 April 1979 to 20 August 1979. Specimen coated on wetted surface only.

CONCLUSIONS AND RECOMMENDATIONS

Of all the germanium specimens tested the least deterioration and decrease in transmittance was exhibited by specimens protected by multilayer AR coating Exotic Materials 40100. Based on the results of this experimental study, it can be concluded that this coating will protect germanium surfaces against corrosive action of seawater for at least 6 months without any significant decrease in its antireflective properties. If minor pitting and a 10-percent decrease in transmittance can be operationally tolerated, the scheduled replacement period can be extended from 6 to 12 months.

The solid chalcogenide glass specimens exhibited no surface deterioration or decrease in transmittance after 4 months of submersion. Based on this observation, it can be concluded that IR windows fabricated from chalcogenide glass have a significantly better resistance to corrosive action of seawater than germanium windows coated with best available multilayer or single-layer AR coatings. Chalcogenide glass windows will withstand continuous or intermittent submersion in seawater in excess of 12 months without any deterioration of wetted surfaces or decrease in transmittance.

1. Multilayer AR coatings should be specified in preference over monolayer AR coatings because they provide superior protection for germanium windows exposed to seawater. Since the corrosion resistance of AR coatings varies, a composition should be specified whose performance under prolonged exposure to seawater environment has been experimentally established, and whose service life has been found to be adequate for the particular application.

2. Environmental tests invoked by MIL-C-675 and/or MIL-C-48497 are not satisfactory predictors for long-term durability of coatings in marine environment. A new military specification should be developed specifically for coatings protecting germanium optics from the corrosive effect of seawater.

3. An R&D program should be initiated that will focus on the application of chalcogenide glasses for IR window systems in marine environment. The aim of the R&D program should be twofold:

   a. Determine the structural properties of chalcogenide glass and define for the benefit of designers safe working stresses to which chalcogenide glass windows may be subjected.

   b. Develop techniques for depositing thick layers of chalcogenide glass on germanium substrata and determine its optical and physical properties after long-term submersion in seawater.

The reason for the twofold approach is that if chalcogenide glass is found to have inadequate strength for service as pressure-resistant windows, it may be utilized in the form of a corrosion-resistant overlay on germanium windows.

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2. NOSC Technical Note 121, "Undersea Testing of IR Anti-reflective Coating and IR Materials," by J.N. Ferrer, March, 1979.

3. J.D. Stachiw and D.L. Endicott, Jr., "Material and Design Considerations for Thermal Imager Windows in Marine Service," Proceedings, Oceans 79, IEEE Publication 79CH1478 & OEC.

4. J.D. Stachiw, "Design Parameters for Germanium Windows Under Uniform Pressure Loading," Proceedings of the Society of Photo-Optical Instrumentation Engineers, Vol. 131, January 1978.

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